A METHOD OF SOLVING SETS OF NONLINEAR ALGEBRAIC EQUATIONS

Progress Report No. 5

March 10, 1968

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Grant No. NGR-36-003-021

Prepared for

National Aeronautics and Space Administration

Washington, D. C. 20546

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Research Report No. March-10-68

by

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FOREWARD

The research reported here is part of the activity of the Chemical Engineering Science Division. The Division's teaching and research efforts are directed toward an understanding and synthesis of processes and materials which involve chemistry as well as engineering. These include the broad areas of reactions, separations, and chemical and physical structure. A general description of the Division's activities is given by CHEMICAL ENGINEERING SCIENCE AT CASE WESTERN RESERVE UNIVERSITY, a report issued in September of each year.

Research activities are sponsored by agencies of the U. S. Government and industrial companies. Duplicate copies of all research reports are automatically issued to companies who participate in the Chemical Engineering Science Industrial Sponsors Program. At the present time, Pittsburgh Plate Glass Company--Chemical Division has joined this newly organized program.

Robert J. Adler
Head
Chemical Engineering Science Division

ABSTRACT

The second generation computer program being developed as part of this research program has been applied to a problem from the field of nuclear magnetic resonance spectroscopy. The program incorporates the supplementary techniques of partitioning and some limited forms of factoring together with an improved algorithm for eliminating polynomial variables. The problem solved consisted of five multivariate polynomial equations, four nonlinear and one linear, in five variables. Twelve real solutions, which are permulations of two "true solutions," were shown to exist. The problem illustrates the capabilities of the second generation program and the usefulness of supplementary techniques.

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1. INTRODUCTION

This report is the fifth semi-annual progress report made by Case Western Reserve University under NASA Research Grant NGR-36-003-021 entitled "A Method of Solving Sets of Nonlinear Algebraic Equations." The research seeks to develop and evaluate combined algebraic and numerical procedures for the computer solution of systems of multivariate polynomial equations. Previous Progress Reports[1] have discussed the results obtained with a first generation computer program and developments underlying a second generation computer program. This report describes the results of applying the second generation computer program now being completed to the solution of a problem in nuclear magnetic resonance (NMR) spectroscopy.

2. PROBLEM DESCRIPTION

Through the analysis of NMR spectral data it is possible to obtain the values of certain parameters which are of considerable value to structural organic and inorganic chemists. These parameters, called chemical shifts and spin-spin coupling constants, are intimately related to the electronic and nuclear configurations of molecules. Postulated structures can often be confirmed or excluded solely from NMR spectra.

The conventional technique for analysis of NMR spectra is an iterative one, where the spin parameters are initially estimated and iteratively improved until the calculated and experimental spectra are brought into agreement. Convergence and uniqueness are usually problems. When more than one or two parameters are involved, it is difficult and costly to seek all of the possible solutions and impossible to be sure that the correct one has been found.

An alternative procedure researched by Professor Whitman[2] in the Chemistry Department at Case Western Reserve University consists of deducing from quantum-mechanical rules an idealized spectrum which agrees with the main features of the experimental spectrum. The spin parameters are then determined so that the calculated and idealized spectra agree precisely; in practice only the line positions are matched. In many interesting cases explicit equations are obtained for the spin parameters in terms of the experimental NMR spectral line positions. However, in several of the most interesting cases[3] this technique produces a system of nonlinear equations in the NMR spin parameters.

In particular, the general three-proton system (called the ABC case) yields a system of five equations--four of which are nonlinear--in the five-spin parameters x_1, x_2, x_3, y_1 and y_2:

$$\begin{cases} x_1 + x_2 + x_3 = c_1 & \text{(1a)} \\ x_1(y_1 - 2y_2) + x_2(y_2 - 2y_1) + x_3(y_1 + y_2) = c_2 & \text{(1b)} \\ \frac{2}{3}(y_1^2 + y_2^2 - y_1y_2) - \frac{3}{2}(x_1x_2 + x_1x_3 + x_2x_3) = c_3 & \text{(1c)} \\ x_1(y_1 - 2y_2)^2 + x_2(y_2 - 2y_1)^2 + x_3(y_1 + y_2)^2 = c_4 & \text{(1d)} \\ 2(y_1 - 2y_2)(y_2 - 2y_1)(y_1 + y_2) = c_5 & \text{(1e)} \end{cases}$$

For the specific ABC system vinyl chloride, the experimentally determined constants, which are functions of the line positions, are:

$$\begin{cases} c_1 = -20.432 \\ c_2 = 1161.711 \\ c_3 = 1284.545 \\ c_4 = -36507.222 \\ c_5 = 378712.368 \end{cases}$$

(The number of significant figures shown are not justified by experimental accuracy. However, these constants were employed in order to facilitate the comparison of Professor Whitman's solution and our solutions.)

Using iterative numerical techniques, Professor Whitman found one solution. Because of difficulty experienced in obtaining convergence, and because it was suspected that more than one solution might exist, the problem was brought to our attention.

3. SOLUTION BY ELIMINATION

The second generation program under development was applied to solve this problem in two different ways. In the first method of solution, only the modified van der Waerden's elimination algorithm[4] was used. The program eliminated the variables x_1, x_2, x_3, and y_1, in that order, to yield a univariate polynomial of 30th degree in y_2. A first attempt to solve this final polynomial failed because of overflow. Rescaling the problem by substituting $y_2 = 10y_2'$ resolved this difficulty. Twelve real solutions were found to exist as listed in Table I.

Set	x_1	x_2	x_3	y_1	y_2
1.	-9·28115	1·47651	-12·6274	-47·9895	-4·23412
2.	1·47651	-12·6274	-9·28115	4·23412	-43·7554
3.	-12·6274	-9·28115	1·47651	43·7554	47·9895
4.	-9·28115	-12·6274	1·47651	47·9895	43·7554
5.	-12·6274	1·47651	-9·28115	-43·7554	4·23412
6.	1·47651	-9·28115	-12·6274	-4·23412	-47·9895
7.*	1·45397	-7·11808	-14·7679	-2·53189	-46·9489
8.	-7·11808	-14·7679	1·45397	46·9489	44·4170
9.	-14·7679	1·45397	-7·11808	-44·4170	2·53189
10.	1·45397	-14·7679	-7·11808	2·53189	-44·4170
11.	-14·7679	-7·11808	1·45397	44·4170	46·9489
12.	-7·11808	1·45397	-14·7679	-46·9489	-2·53189

Table I Solutions to NMR Spectroscopy Problem

* Solution found by Professor Whitman using iterative numerical methods.

These twelve solutions are permutations of two different sets of spin parameters. The first six solutions correspond to permutations of one set of spin parameters, while the last six are permutations of the second set. Both sets of spin parameters are in precise agreement with the observed spectral line positions. However, the two sets yield different intensities. In this particular problem the second set, which was found by Professor Whitman, more closely matches the experimental intensities. Using double-precision arithmetic, the total computing time was 535 seconds. The maximum number of list cells employed simultaneously during the computation was 1064. Together with other auxiliary data structures, the peak number of memory words employed for data storage was about 8,000 words.

4. SOLUTION BY SUPPLEMENTARY TECHNIQUES COMBINED WITH ELIMINATION

A second more efficient method of solution made use of the supplementary techniques of grouping and partitioning. The steps of the second solution are now described in detail. After eliminating x_1 and x_2, the equations become:

$$\begin{cases} x_1 + x_2 + x_3 = c_1 & (2a) \\ x_1(y_1 - 2y_2) + x_2(y_2 - 2y_1) + x_3(y_1 + y_2) = c_2 & (2b) \end{cases}$$

$$\begin{cases} \frac{27}{2}x_3^2(y_1^2 + y_2^2 - y_1y_2) - \frac{9}{2}x_3[2c_1(y_1^2 + y_2^2 - y_1y_2) + c_2(y_1 + y_2)] \\ \quad + \frac{3}{2}[c_2 - c_1(y_1 - 2y_2)][c_2 - c_1(y_2 - 2y_1)] \\ \quad + 6(y_1 - y_2)^2(y_1^2 + y_2^2 - y_1y_2) = 9c_3(y_1 - y_2)^2 & (2c) \\ 9x_3y_1y_2 - c_1(y_1 - 2y_2)(y_2 - 2y_1) - c_2(y_1 + y_2) = c_4 & (2d) \\ 2(y_1 + y_2)(y_1 - 2y_2)(y_2 - 2y_1) = c_5 & (2e) \end{cases}$$

The symmetry of y_1 and y_2 in the subsystem (2c), (2d) and (2e) suggested the following groups:*

$$\begin{cases} P = y_1y_2 \\ Q = y_1 + y_2 \end{cases} \qquad (3)$$

Introducing P and Q into (2c), (2d) and (2e) by hand and appending system (3) to (2) yields the following partitionable system.

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*Other useful groups also exist. For example, $P' = (y_1 - 2y_2) + (y_2 - 2y_1)$ and $Q' = (y_1 - 2y_2)(y_2 - 2y_1)$.

$$\begin{cases} x_1 + x_2 + x_3 = c_1 \\ x_1(y_1 - 2y_2) + x_2(y_2 - 2y_1) + x_3(y_1 + y_2) = c_2 \end{cases} \tag{4a}$$

$$\begin{cases} \frac{27}{2}x_3^2(Q^2 - 3P) - \frac{9}{2}[2c_1(Q^2 - 3P) + c_2Q] \\ \qquad + \frac{3}{2}[c_2^2 + c_1c_2Q - c_1^2(2Q^2 - 9P)] \\ \qquad + 6(Q^2 - 4P)(Q^2 - 3P) = 9c_3(Q^2 - 4P) \\ 9x_3P + c_1(2Q^2 - 9P) - c_2Q = c_4 \\ 2Q(9P - 2Q^2) = c_5 \end{cases} \tag{4b}$$

$$\begin{cases} P = y_1y_2 \\ Q = y_1 + y_2 \end{cases} \tag{4c}$$

The subsystem (4b) can be solved by eliminating first x_3 and then P to obtain a 12th degree polynomial in Q. This polynomial in Q has six real solutions, each of which gives rise to a (x_3, P, Q) solution to (4b). Each of these sets when substituted into (4c) yields a pair of (x_3, y_1, y_2, P, Q) solutions to (4b,c). Each of these (x_3, y_1, y_2, P, Q) solutions when substituted into (4a) yields a (x_1, x_2, x_3, y_1, y_2, P, Q) solution for the entire problem (4). All twelve of these solutions satisfy (1) and are in agreement with the solutions of Table I to at least seven significant figures.

This method of solution, employing the supplementary techniques of grouping and partitioning combined with elimination, required only 161 seconds of computing time and a peak number of list cells of 214.

5. CONCLUDING REMARKS

From the standpoint of NMR spectroscopy, this capability of finding all solutions, in this case a "double" solution, is of considerable importance, since many workers have neglected the possibility of multiple solutions. The method of solution being developed in this research will, among other things, be of significant practical value to NMR spectroscopists, since it will permit the analysis of NMR spectra to be performed unambiguously for ABC, ABCD, etc., systems. It should be emphasized that the method provides essentially the only means of determining the uniqueness, and thus the reliability, of spectral analyses for such systems.

The example presented is representative of the capabilities of the second generation computer program as it presently exists; approximately four nonlinear variables can be handled in typical cases by using elimination only. This example also serves to illustrate the usefulness of supplementary techniques, which can increase the size of problems that can be handled. The most critical computing factor is memory space. Propagation of round-off errors and computing time do not appear to be as critical. Further development of supplementary techniques and the availability of larger memories will permit somewhat larger problems to be treated in the future.

6. PERSONNEL

Personnel associated with the research during the last six-month period include Professor R. J. Adler and graduate students S. Y. Ku, C. G. Sperling and W. R. Brown. Mr. Ku is a Ph.D. candidate and Messrs. Sperling and Brown are M.S. candidates. All three of these men will be writing theses during 1968.

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A METHOD OF SOLVING SETS OF NON-LINEAR ALGEBRAIC EQUATIONS (Prog. Rep. No. 5) Chem. Eng. Sci. Report No. 03-10-68

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